



PCT/AU03/01364
Rec'd PCT/PTO 15 APR 2005

REC'D 11 NOV 2003

WIPO

PCT

**PRIORITY
DOCUMENT**

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Patent Office
Canberra

#2

I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2002952083 for a patent by BHP BILLITON INNOVATION PTY LTD as filed on 16 October 2002.



WITNESS my hand this
Fourth day of November 2003

J. Billingsley

JULIE BILLINGSLEY
TEAM LEADER EXAMINATION
SUPPORT AND SALES

BEST AVAILABLE COPY

AUSTRALIA
Patents Act 1990

PROVISIONAL SPECIFICATION

Applicant(s):

BHP BILLITON INNOVATION PTY LTD

A.C.N. 008 457 154

Invention Title:

MINIMISING CARBON TRANSFER IN AN ELECTROLYTIC CELL

The invention is described in the following statement:

MINIMISING CARBON TRANSFER IN AN ELECTROLYTIC CELL

The present invention relates to electrochemical reduction of metal oxides.

5

The present invention was made during the course of an on-going research project on the electrolytic reduction of titania (TiO_2) carried out by the applicant.

10

During the course of the research project the applicant carried out experimental work on an electrolytic cell that included a graphite crucible that formed an anode of the cell, a pool of molten CaCl_2 -based electrolyte in the crucible, and a cathode that included solid titania.

15

The CaCl_2 -based electrolyte was a commercially available source of CaCl_2 , namely calcium chloride dihydrate, that partially decomposed on heating and produced CaO .

20

The applicant operated the electrolytic cell at a potential above the decomposition potential of CaO and below the decomposition potential of CaCl_2 .

25

The applicant found that the cell could electrochemically reduce titania to titanium with very low concentrations of oxygen.

30

The applicant does not have a clear understanding of the electrolytic cell mechanism at this stage. Nevertheless, whilst not wishing to be bound by the comments in this paragraph, the applicant offers the following comments by way of an outline of a possible cell mechanism. The experimental work carried out by the applicant produced evidence of Ca metal in the electrolyte. The applicant believes that, at least during

35

the early stages of operation of the cell, the Ca metal was the result of electrodeposition of Ca^{++} cations as Ca metal on electrically conductive sections of the cathode. The experimental work was carried out using a CaCl_2 -based electrolyte at a cell potential below the decomposition potential of CaCl_2 . The applicant believes that the initial deposition of Ca metal on the cathode was due to the presence of Ca^{++} cations and O^{--} anions derived from CaO in the electrolyte. The decomposition potential of CaO is less than the decomposition potential of CaCl_2 . In this cell mechanism the cell operation is dependent at least during the early stages of cell operation on decomposition of CaO , with Ca^{++} cations migrating to the cathode and depositing as Ca metal and O^{--} anions migrating to the anode and forming CO and/or CO_2 (in a situation in which the anode is a graphite anode). The applicant believes that the Ca metal that deposited on electrically conductive sections of the cathode was deposited predominantly as a separate phase in the early stages of cell operation and thereafter dissolved in the electrolyte and migrated to the vicinity of the titania in the cathode and participated in chemical reduction of titania. The applicant also believes that at later stages of the cell operation part of the Ca metal that deposited on the cathode was deposited directly on partially deoxidised titanium and thereafter participated in chemical reduction of titanium. The applicant also believes that the O^{--} anions, once extracted from the titania, migrated to the anode and reacted with anode carbon and produced CO and/or CO_2 and released electrons that facilitated electrolytic deposition of Ca metal on the cathode.

However, notwithstanding that the cell could electrochemically reduce titania to titanium with very low concentrations of oxygen, the applicant also found that there were relatively significant amounts of carbon transferred from the anode to the electrolyte and to the

titanium produced at the cathode under a wide range of cell operating conditions. Carbon in the titanium is an undesirable contaminant. In addition, carbon transfer was responsible for low current efficiency of the cell because
5 of back reactions involving calcium metal that is dissolved in the electrolyte and CO and/or CO₂ gas that is generated at the anode. Both of these problems are significant barriers to commercialisation of the electrochemical reduction technology.

10

The applicant carried out experimental work to identify the mechanism for carbon transfer and to determine how to minimise carbon transfer and/or to minimise the adverse effects of carbon transfer.

15

The experimental work indicated that the mechanism of carbon transfer is electrochemical rather than erosion and that one way of minimising carbon transfer, and therefore minimising contamination of
20 titanium produced at the cathode by electrochemical reduction of titania at the cathode, is to position a membrane between the anode and the cathode that is:

(a) impermeable to carbon in ionic and non-ionic
25 forms to prevent migration of carbon from the anode to the cathode, and

(b) permeable to oxygen anions so that the anions
can migrate from the cathode to the anode.

30

Australian provisional application PS1170 in the name of the applicant describes this invention.

Specifically, the Australian provisional
35 application describes an invention of an electrolytic cell for electrochemical reduction of a metal oxide, such as titania, in a solid state, which electrolytic cell

includes an anode formed from carbon, a cathode formed at least in part from the metal oxide, and a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms positioned between the cathode and the anode to thereby prevent migration of carbon to the cathode.

In the course of experimental work on a membrane made of yttria stabilised zirconia the applicant noted that, over time, there was break-down of sections of the membrane in direct contact with the electrolyte. This a potentially serious problem.

The applicant believes that the break-down may be due to reduction of zirconia by calcium metal dissolved in the electrolyte. The applicant also believes that there may be no discernible reduction of yttria by calcium or other constituents of the electrolyte.

As a consequence of the above, the present invention provides an electrolytic cell for electrochemical reduction of a metal oxide in a solid state, which electrolytic cell includes a molten electrolyte, an anode formed from carbon in contact with the electrolyte, a cathode formed at least in part from the metal oxide in contact with the electrolyte, and a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms positioned between the cathode and the anode to thereby prevent migration of carbon from the anode to the cathode, the membrane includes a body and an outer lining on the surface of the body on the cathode side of the membrane, and the outer lining is formed from a material that is inert with respect to dissolved metal in the electrolyte and is impermeable to the dissolved metal.

In a situation in which the metal oxide is

titania it is preferred that the electrolyte be a CaCl_2 -based electrolyte that includes CaO . In this situation the dissolved metal is calcium metal. In this situation preferably the outer lining is formed from a material that
5 is inert and impermeable with respect to calcium metal.

Preferably the anode is formed from graphite.

The membrane may be formed from any suitable
10 material(s).

Preferably the body of the membrane is formed from a solid electrolyte.

15 Preferably the solid electrolyte is an oxide.

One suitable solid electrolyte tested by the applicant is yttria stabilised zirconia.

20 The outer lining may be formed from any suitable material.

Preferably the outer lining is formed from an
oxide.

25 Preferably the material for the outer lining is a rare earth oxide.

More preferably the rare earth oxide is yttria.

30 Preferably the lining is continuous and covers all of the surface of the body of the membrane that would otherwise be in contact with the electrolyte so that there are no sections of the body that are in contact with the
35 electrolyte on the cathode side of the membrane.

Preferably, the cathode also includes an

electrical conductor.

The present invention also provides a method of electrochemical reduction of a metal oxide using the
5 above-described electrolytic cell.

Preferably, the method includes a step of operating the cell at a potential that is above a decomposition potential of at least one of the
10 constituents of the electrolyte so that there are cations of a metal other than that of the metal oxide in the electrolyte.

In a situation in which the metal oxide is a
15 titanium oxide, such as titania, it is preferred that the electrolyte be a CaCl_2 -based electrolyte that includes CaO as one of the constituents.

In such a situation it is preferred that the cell
20 potential be above that the decomposition potential for CaO .

It is preferred that the cell potential be above
25 1.5 V.

The CaCl_2 -based electrolyte may be a commercially available source of CaCl_2 , such as calcium chloride dihydrate, that partially decomposes on heating and produces CaO or otherwise includes CaO .
30

Alternatively, or in addition, the CaCl_2 -based electrolyte may include CaCl_2 and CaO that are added separately or pre-mixed to form the electrolyte.

35 The present invention is described further with reference to the accompanying drawing which illustrates in schematic form a preferred embodiment of an electrolytic

cell in accordance with the present invention.

Whilst the following description relates to electrochemical reduction of titania, the basic principle is equally applicable to other metal oxides, in particular oxides of silicon and germanium or alloys containing these metals.

The cell includes a graphite crucible 10 that forms an anode 10 of the cell, a pool 14 of molten CaCl_2 -based electrolyte that contains at least some CaO in the crucible, and a basket 16 of titania pellets connected to a lower end of a Kanthal or stainless steel wire 18 that form a cathode 20 of the cell.

The molten electrolyte contacts the anode 10 and the cathode 22.

The cell further includes a power source 22 and electrical connections between the power source 22 and the anode 10 and the cathode 20.

The electrical connections include the above-described wire 18 and an electrically conductive wire that connects the power source 22 and the anode 10.

The cell further includes a membrane 28 that is positioned between the anode 10 and the cathode 20. The membrane divides the cell into an cathode chamber 36 and an anode chamber 38.

The membrane includes a body 32 of yttria stabilised zirconia and an inner lining 34 of yttria.

Yttria stabilised zirconia and yttria are permeable to oxygen anions and therefore the membrane 28 does not interfere with migration of oxygen anions from

the cathode to the anode.

In addition, yttria is inert with respect to the constituents of the electrolyte (including dissolved calcium metal in the electrolyte) and is impermeable to calcium metal. The yttria lining 34 is provided to prevent contact between calcium metal in the cathode chamber 36 and yttria stabilised zirconia of the body 32.

In use, the above-described electrolytic cell 2 is positioned in a suitable furnace to maintain the electrolyte in a molten state. The atmosphere around the crucible 10 is preferred to be an inert gas, such as argon, that does not react with the molten electrolyte.

Once the cell reaches its operating temperature, a preselected voltage above the decomposition potential of CaO in the electrolyte is applied to the cell, whereby reduction of the titania in the cathode is carried out as described above.

The oxygen anions that pass into the electrolyte 18 by virtue of electrochemical reduction of the metal oxide migrates to the anode 10 via the electrolyte and by passing through the membrane 16 and dissolves in the molten metal. The oxygen anions give up electrons at the anode and CO/CO_2 gas evolves at the anode.

Calcium metal that forms at the cathode 20 and thereafter dissolves in the electrolyte diffuses through the cathode chamber 36. However, the membrane 32 prevents the calcium metal migrating into the anode chamber 38 and thereby avoids undesirable back reaction of calcium metal and CO/CO_2 .

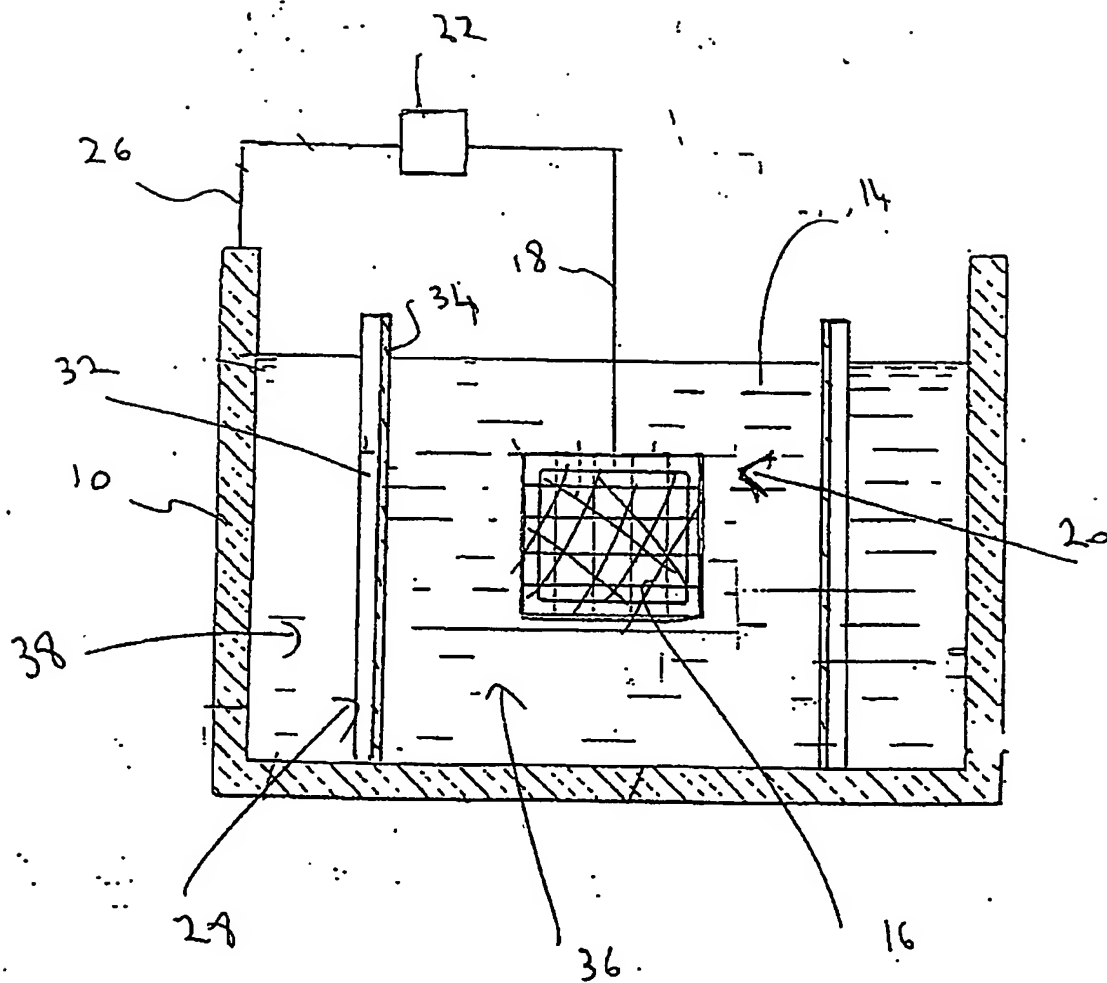
In addition, the yttria lining 34 of the membrane 32 prevents the calcium metal contacting and breaking down

the zirconia in the body 32 of the membrane 28.

Many modifications may be made to the present invention as described above without departing from the spirit and scope of the invention.

By way of example, whilst the above description of the invention focuses on electrochemical reduction of titania, the invention is not so limited and extends to electrochemical reduction of other titanium oxides and to oxides of other metals and alloys. Examples of other potentially important metals are aluminium, silicon, germanium, hafnium, magnesium, and molybdenum.

Furthermore, whilst the above description focuses on CaCl_2 -based electrolyte, the invention is not so limited and extends to any other suitable electrolytes. Generally, suitable electrolytes will be salts and oxides that are soluble in water. One example of a potentially suitable electrolyte is BaCl_2 .



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.